Shaping the fluorescence emission by cavity plasmons in dielectric-metal core-shell resonators

Zhi-Qin Li, Chi Zhang, Ping Gu, Mingjie Wan, Peng Zhan, Zhuo Chen, and Zhenlin Wang

Citation: Applied Physics Letters 107, 251105 (2015); doi: 10.1063/1.4938393
View online: http://dx.doi.org/10.1063/1.4938393
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/107/25?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in

Experimental observation of sharp cavity plasmon resonances in dielectric-metal core-shell resonators

Preparation and properties of noble metal core/shell nanostructures prepared by excimer laser ablation in liquid solutions
J. Laser Appl. 26, 022001 (2014); 10.2351/1.4858315

Highly efficient and tunable fluorescence of a nanofluorophore in silica/metal dual shells with plasmonic resonance
J. Appl. Phys. 103, 024301 (2008); 10.1063/1.2830986

Indirect absorption and direct fluorescence detections in the field of a resonantly excited surface plasmon

Scattering analysis of inhomogeneously dielectric-filled cavities
Shaping the fluorescence emission by cavity plasmons in dielectric-metal core-shell resonators

Zhi-Qin Li,1 Chi Zhang,1 Ping Gu,1 Mingjie Wan,1 Peng Zhan,1,2 Zhuo Chen,1,2,a) and Zhenlin Wang1,2,b)

1School of Physics and National Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093, China
2Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210093, China

(Received 3 November 2015; accepted 3 December 2015; published online 22 December 2015)

We observe experimentally the spectral and spatial reshaping of fluorescence emission in dye-doped dielectric-metal core-shell resonators that support multipolar electric and magnetic-based cavity plasmon resonances. By comparing the experimental fluorescence spectra with analytical calculations based on Mie theory, we are able to demonstrate that the strong reshaping effects are the results of the coupling of dye molecules to those narrow-band cavity plasmon resonances. In addition, we show that the polarization of the fluorescence emission can also be modified by selectively coupling the molecules to the magnetic or electric based cavity plasmons. © 2015 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [http://dx.doi.org/10.1063/1.4938393]

Metallic nanostructures supporting collective electron excitations, known as surface plasmon resonances (SPRs), have the ability to concentrate light into subwavelength volumes and produce highly localized fields and large enhancement of local optical density of states.1 When light emitters such as quantum dots and organic dyes are positioned in the vicinity of metallic nanostructures, strong near-field interactions may occur between the excited emitters and the SPRs, which provide a unique opportunity for enhancing the magnitude of the fluorescent response of these emitters;2–7 manipulating the fluorescence lifetime;8–10 reshaping the emission spectrum;11–16 and even controlling the far field angular distribution, polarization, and coherence of the emission.17–27 In those earlier studies of the reshaping of the emission by dye molecules, localized SPRs supported by individual metallic nanostructures usually exhibit low quality factors,11–13,18,24 and consequently, only the reshaped fluorescence spectra with broad linewidths are observed. Although high-quality-factor hybrid photonic-plasmon propagating modes supported by periodic plasmonic structures, such as periodically patterned metal nanoparticles or dielectric sphere arrays deposited on a flat metal layer,15,16,25–27 have been reported to produce spectrally narrow fluorescence emission peaks, they are based on the diffractive coupling mechanism and thus are extremely sensitive to the incident angles. Recently, dipolar cavity plasmon modes supported on the metal semi-shells have also been shown to be apt to direct the fluorescence from the dyes contained in their dielectric cores into the forward direction.26 As compared to the metal semi-shells, their full-shell counterparts are capable of supporting cavity plasmons with much higher quality factors29,30 and would, thus, be expected to modify the fluorescence emission more dramatically and efficiently.

In this paper, we investigate experimentally the fluorescence reshaping effect in dielectric-metal core-shell resonators (DMCSRs). By wrapping a nearly perfect metal shell layer around a dye-doped dielectric sphere, the coupling of the dye molecules to a set of sharp electric and magnetic-based Mie cavity plasmon resonances supported by DMCSRs is enabled. As a result, a strong modification of the fluorescence emission spectrum is experimentally observed. In addition to the spectral reshaping, we further demonstrate that the fluorescence emission can be spatially redirected in completely different radiation patterns and different polarizations that correspond to the different multipolar cavity plasmon resonances. These unique emission properties make the dye-doped DMCSRs attractive candidates for applications in fluorescence sensing and low-threshold lasing.

High-quality DMCSRs with a nearly perfect silver shell are prepared using a simple two-step approach we recently developed which allows for the creation of core-shell structures with various core sizes consisting of virtually any metal and dielectric materials.31 In brief, a monolayer of self-supporting dye-doped polystyrene (PS) spheres with a diameter of 1.0 μm (Thermo-Scientific, dye-type: Firefli Fluorescent Red, central emission wavelength at 612 nm) is formed onto a substrate with tens of micrometer-sized through-holes and followed by two successive silver depositions onto the upper and lower half-surfaces of the PS spheres to wrap a nearly-perfect silver shell layer around each colloid. A representative scanning electron microscopy (SEM) image of the resultant DMCSRs is shown in Fig. 1(a). Noting that the thickness of the silver shell layer in this study is chosen to be ~40 nm, which is beyond the optical skin depth of ~20 nm for silver in the range of visible, so that the DMCSR can effectively act as a closed metallic cavity.31

The fluorescence emission properties of the dye-doped DMCSRs are characterized using a homebuilt photoluminescence setup [Fig. 1(b)]. Light from a 488 nm wavelength diode laser with ~15 μW power is slightly focused to a spot...
of $\sim 20 \mu m$ onto the samples to pump the dye molecules, and its linear polarization can be rotated by a half-wave plate. The transmitted optical signals pass through a long pass edge filter to block the pump light and then are collected by an objective ($50 \times$, 0.7 N. A.). After a tube lens L1, an optical fiber is placed on its focal plane, where the real image of the sample appears, to guide the fluorescence signals into a grating spectrometer, outputting energetically resolved (spatially integrated) fluorescence emission spectra. With a second lens L2, the back focal plane of the objective, which is a Fourier image of the radiation from the sample, can be imaged directly at the entry slit of a charged coupled device (CCD) imaging spectrometer to generate fluorescence intensity maps as functions of both wavelengths and emission angles. In the measurements, the $\Gamma\times X$ direction of the array of DMCSRs [Fig. 1(a)] is aligned parallel to the entry slit of the spectrometer (vertical direction).

The energy-resolved fluorescence spectra of the DMCSRs pumped by normally incident laser with its linear polarization along the $\Gamma\times J$ and $\Gamma\times X$ directions are first measured at the focal plane of the tube lens L1 and shown in Fig. 1(c), which are normalized with a fluorescence emission spectrum collected on the self-supporting dye-doped PS sphere array [inset in Fig. 1(c)]. Figure 1(c) presents that the results are almost exactly the same regardless of the incident electric field orientations of the pump laser. The most remarkable spectral features are several sharp emission peaks. Our previous experimental studies have already demonstrated that the plasmonic properties of the prepared DMCSRs are dominated by a set of magnetic and electric-based cavity plasmons with their optical fields being tightly confined within the dielectric cores.\textsuperscript{31} Such highly localized nature prevents the cavity plasmons in adjacent DMCSRs from interacting with each other. Therefore, even though the DMCSRs are closely packed like in this study, the cavity plasmons are allowed to be analyzed using Mie theory. One of the main advantages of the analytical Mie solution is its ability to decompose the obtained spectra into separate multipolar contributions, characterized by electric TM($l,n$) and magnetic TE($l,n$) scattering coefficients, where $l$ is the index of angular momentum and $n$ is the order of the mode.\textsuperscript{32} Results of this analysis on the absorption efficiency of the individual DMCSR composed of a 1000-nm-diameter PS sphere concentrically surrounded by a uniform 40-nm-thick silver shell are shown in Fig. 1(d). In the calculations, the refractive index of PS is assumed to be 1.59, and the permittivity of silver is taken from the experimental data by Johnson and Christy.\textsuperscript{33} By comparing Figs. 1(c) and 1(d), it is directly seen that there is a very good one-to-one correspondence between experimentally observed fluorescence emission peaks and theoretically predicted absorption peaks, providing strong evidence that the dramatic modification of the fluorescence emission spectrum is due to the near-field coupling of the dyes to multipolar sharp Mie cavity plasmon resonances.

In order to gain insight not only in the spectral reshaping of the fluorescence emission but also in the directional reshaping, the normalized angle-resolved fluorescence spectrum of the DMCSRs pumped by normally incident laser with its linear polarization along the $\Gamma\times X$ direction is detected at the focal plane of the lens L2 (the Fourier image) and shown in Fig. 2(a). Again, as indicated by the dashed lines, at each wavelength of the theoretically predicted absorption peaks, a fluorescence emission enhancement is clearly observed. Moreover, these emission enhancements show up as verticals in the angle-resolved fluorescence spectrum, indicating highly localized nature of the cavity plasmon resonances.\textsuperscript{34} More importantly, Fig. 2(a) demonstrates that the fluorescence emission enhanced by different cavity plasmon resonances exhibits different angular distributions. For example, the fluorescence emission associated with the TM($1,3$) cavity plasmon resonance is mostly radiated into the forward direction. On the contrary, when the dye molecules are coupled to the TE($4,1$), TM($3,2$), TE($2,2$), and TE($5,1$) cavity plasmon resonances, the forward radiation could be strongly suppressed, and most of the emission energy is funneled aside the forward direction, giving rise to a pronounced lateral radiation. Figures 2(b) and 2(c) show the radiation patterns of the fluorescence emission at the TM($1,3$) and TM($3,2$) cavity plasmon resonances, respectively. It is seen that the angular widths of the forward directional emission and the laterally emitted fluorescence beam...
could be as narrow as \( \sim 20^{\circ} \) and \( \sim 10^{\circ} \), respectively. It is worth noting that with such spatial reshaping effects, the energetically un-resolved broad emission peaks could be clearly resolved in the angular distributed spectrum. For example, the dyes coupled to two spectrally overlapped TM\((1,3)\) and TE\((5,1)\) cavity plasmon resonances only show a merged broad peak around 565 nm in the energy-resolved fluorescence spectrum [Fig. 1(c)], while the forward and lateral radiation patterns associated with these two resonances can be clearly identified in the angle-resolved emission spectrum [Fig. 2(a)].

In the following, we demonstrate that the polarization states of the fluorescence emission can also be modified by coupling the dyes to the multipolar cavity plasmon resonances. To analyze the polarization of the fluorescence emission, a linear polarizer is placed before the entry slit of the spectrometer. Figures 3(a) and 3(b) show, respectively, the angle-resolved fluorescence spectra through this linear polarizer with its axis oriented parallel and normal to the entry slit, in which the DMCSRs are pumped by normally incident laser with its polarization along the \(-X\) direction. The dashed lines indicate the resonance wavelengths of the theoretically predicted cavity plasmons.

In summary, high quality DMCSRs composed of a spherical dye-doped dielectric core and a nearly perfect silver shell layer are prepared by a recently developed method. By coupling the dye molecules to the sharp cavity plasmon resonances of the DMCSRs, the fluorescence emission spectrum is strongly modified and has a good one-to-one correspondence with the theoretically predicted resonance positions. The fluorescence emission can also be spatially reshaped with different polarizations dependent on the multipolar magnetic or electric-based cavity plasmon resonances. These fluorescence reshaping effects in the dye-doped DMCSRs may find useful applications in optical router, fluorescence sensing, and low-threshold lasing.

The authors thank the support by the State Key Program for Basic Research of China (SKPBR) under Grant Nos. 2012CB921501 and 2013CB632703, and the National Nature Science Foundation of China (NSFC) under Grant Nos. 11174137, 91221206, 11274160, 11321063, and 51271092.
